DIESEL EXHAUST PARTICULATES*

First Listed in the *Ninth Report on Carcinogens*

CARCINOGENICITY

Exposure to diesel exhaust particulates is *reasonably anticipated to be a human carcinogen,* based on findings of elevated lung cancer rates in occupational groups exposed to diesel exhaust (IARC, 1989; Cohen and Higgens, 1995; Bhatia *et al.*, 1998) and supporting animal and mechanistic studies. An increased risk of lung cancer is found in the majority of human studies. The overall relative risk is about 1.3, and higher risks are found in more heavily exposed subgroups in some studies. The increased risk is not readily explained by confounding by either smoking or asbestos exposure. However, the increased risk cannot always be clearly ascribed to diesel exhaust exposure. Although some studies employed semiquantitative estimates of diesel exhaust exposure (*e.g.* Steenland *et al.,* 1998), most studies used inadequate measures of exposure.

Studies of the carcinogenicity of diesel exhaust particulates in animals have shown a consistent lung tumor response in rats, but not in the mouse or hamster. The response in rats appears to be due to the particulate component of exhaust, as the filtered vapor phase of exhaust has been shown not to be tumorigenic. Solvent extracts of diesel exhaust particles are carcinogenic when applied to the skin, or administered by intratracheal instillation or intrapulmonary implantation to rats, mice or hamsters.

ADDITIONAL INFORMATION RELAVANT TO CARCINOGENESIS OR POSSIBLE MECHANISM OF CARCINOGENESIS

Diesel exhaust is a complex mixture of combustion products of diesel fuel, with the exact composition depending on the type of engine, the speed and load at which it is run, and the composition of the fuel used. Diesel exhaust contains identified mutagens and carcinogens both in the vapor phase and associated with respirable particles. Diesel exhaust particles are considered likely to account for the human lung cancer findings because they are almost all of a size allowing penetration to the entire lung, and because mutagenic and carcinogenic chemicals including polyaromatic hydrocarbons and nitroarenes have been extracted from these particles with organic solvents, or with a lipid component of mammalian lung surfactant.

While diesel particulate exposures produce lung cancer in rats, the relevance of this result in predicting the human response has been questioned because diesel exhaust particulate exposure produces a characteristic spectrum of inflammatory and neoplastic pulmonary responses in the rat; responses also seen with other inhaled particles of varying toxicity, and apparently little influenced by the chemical constituents of the particles. Although the precise bioavailability of chemical mutagens and carcinogens from inhaled diesel particulates is not known, DNA adducts attributed to diesel exhaust particulate exposures have been demonstrated in the lung of exposed rats. Similarly, lymphocyte-DNA adducts were found higher in several studies of occupational groups exposed to diesel exhaust than in groups with lower or ambient exposures, although diesel exhaust exposure was not quantified in these studies and exposure to used motor oil likely contributed to the adducts observed in one study.

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* There is no separate CAS registry number assigned to Diesel Exhaust Particulates

PROPERTIES

Diesel exhaust is a complex mixture of combustion products of diesel fuel, with the exact composition dependent upon the type of engine, operating conditions, lubricating oil, additives, emission control system, and the composition of the fuel used (Ullman 1989; Obert 1973). Diesel engines are typically separated according to their service requirements light-duty or heavy-duty. Light-duty and heavy-duty diesel engines' operating conditions differ in terms of engine speed, expected load, fuel composition, and engine emission controls. Typically light-duty vehicles such as automobiles and light trucks operate at higher speeds than heavy-duty vehicles such as trucks. The total particulate emission concentration from light-duty diesel engines is much smaller than from heavy-duty diesel engines. In general newer heavy-duty trucks emit diesel particulates at a rate 20 times greater than catalyst-equipped gasoline-fueled vehicles (WHO 1996). However, depending on operating conditions, fuel composition, and engine control technology, light-duty diesel engines can emit 50 to 80 times and heavy-duty diesel engines 100 to 200 times more particulate mass than typical catalytically equipped gasoline engines (McClellan 1986).

The particle size distribution of diesel exhaust is bi-modal with a nuclei mode (0.0075 to 0.042 μm in diameter) and an accumulation mode (0.042 to 1.0 μm in diameter) (Baumgard and Johnson 1996), most of which occur in aerodynamic diameters ranging from 0.1 to 0.25 μm in diameter (Groblicki and Begeman 1979; Dolan et al. 1980; NRC 1982; Williams 1982). Approximately 98 % of the particles emitted from diesel engines are less than 10 microns in diameter, 94 % less than 2.5 microns in diameter, and 92 % less than 1.0 microns in diameter (ARB 1997).

Engines running under low load typically produce fewer particles with a higher proportion of organic compounds associated with the available particle mass. Conversely, engines under high load typically produce more particulate matter with a lower proportion of organic compounds associated with available particles. Kishi et al. (1992) found that exhaust gas temperatures affect particle composition. Low exhaust gas temperatures produce particulate matter with more adsorbed soluble organics than particulate matter produced in a high exhaust gas temperature environment.

The emissions consist of a nonpolar fraction (57%), a moderately polar fraction (9%), and a polar fraction (32%) (Schuetzle 1983; Schuetzle et al. 1985), with the remainder unrecoverable. Diesel engines operate with excess air (~25-30 parts air to 1 part fuel) (Lassiter and Milby 1978). The gas phase fraction is composed primarily of typical combustion gases such as nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), and water vapor (H_2O). As a result of incomplete combustion, the gaseous fraction also contains pollutants such as carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), volatile hydrocarbons, and low molecular weight Polyaromatic hydrocarbons (PAH) and their derivatives.

The inorganic fraction of the particulate phase of diesel fuel combustion emissions primarily consists of small elemental carbon particles ranging from 0.01-0.08 microns in diameter. The organic and elemental carbon accounts for approximately 80% of the total particulate matter mass. The remaining 20% is composed of sulfate (mainly H_2SO_4) (Pierson and Brachaczek 1983) and some inorganic additives and components of fuel and motor oil.

In general, the organic compounds identified in diesel exhaust emissions contain hydrocarbons, hydrocarbon derivatives, PAH, PAH derivatives, multifunctional derivatives of PAH, heterocyclic compounds, heterocyclic derivatives, and multifunctional derivatives of heterocyclic compounds (Schuetzle 1988). The organic fractions consist of soluble organic compounds such as aldehydes, alkanes, alkenes, and high molecular weight PAH and PAH-derivatives.

Because of their high surface area, diesel particulates (DP) are capable of adsorbing relatively large amounts of organic material. The adsorbed elements come from unburned fuel, lubricating oil, and pyrosynthesis during fuel combustion. A variety of mutagens and carcinogens such as PAH and nitro-PAH (see for example NRC 1982; Tokiwa and Ohnishi 1986; WHO 1996) are adsorbed by the particulates. There is sufficient evidence for the carcinogenicity for 15 PAHs (a number of these PAHs are found in diesel exhaust particulate emissions) in experimental animals (NTP 1998) (http://ehis.niehs.nih.gov/roc/). The nitroarenes (five listed) meet the established criteria for listing as "reasonably anticipated to be a human carcinogen" based on carcinogenicity experiments with laboratory animals (NTP 1998) (http://ehis.niehs.nih.gov/roc/). The organic extractable fraction of Diesel Particulates (DP) is typically in the 20-30% range, but may be as high as 90% (Williams *et al.* 1989), depending upon vehicle type and operating conditions. In general, under low load, diesel engine incomplete combustion results in relatively low particle concentrations and a higher proportion of organic associated particles (Dutcher *et al.* 1984).

EPA regulations from 1983-1993, and the Clean Air Act Amendments from 1994-1998, reduced federal emissions standards for nitrogen oxides and particulate matter in diesel exhaust emission, resulting in changes in diesel fuel quality. The contributing factors for diesel particulate emissions are the sulfur and PAH content in fuel. The higher the PAH and/or sulfur content, the higher the particulate emissions. Sulfur content in fuel ranged from 0.3 to 0.24 weight percent at the end of 1993.

A 1993 change in EPA regulations, which required a maximum sulfur content of 0.05 weight percent, resulted in a sharp decline in the fuel sulfur content to 0.03 in 1994. The resulting sulfur oxide concentration in diesel exhaust would be proportional to 88% to 90% from the previous year (API 1998).

USE

There are no known uses of diesel exhaust particulates.

PRODUCTION

Internal combustion engines have been used in cars, trucks, locomotives and other motorized machinery for about 100 years (IARC 1989). The combustion of diesel fuel in a compression ignition engine produces diesel exhaust. Engine exhaust contains thousands of gaseous and particulate substances. There are three major groups of diesel exhaust sources: Mobile sources (on-road vehicles and other mobile sources), stationary area sources (oil and gas production facilities, stationary engines, repair yards, shipyards etc.), and stationary point sources (chemical manufacturing, electric utilities, etc.). The composition and quantity of the emissions from an engine depend mainly on the type and condition of the engine, fuel composition and additives, operating conditions and emission control devices.

EXPOSURE

Various employee groups have been studied to determine their occupational exposures to diesel exhaust particulates (DP). They include railroad workers, mine workers (use diesel-powered equipment), bus garage workers, trucking company workers, fork-lift truck operators, fire-fighters, lumberjacks, toll-booth and parking garage attendants, and many professions servicing or handling automobiles (car mechanics, professional drivers, *etc.*). The National Institute for Occupational Safety and Health (NIOSH) has estimated that approximately 1.35 million workers are occupationally exposed to DP in about 80,000 workplaces in the United States (NIOSH 1989).

Railroad workers' potential for exposure has increased since 1959, when almost all the U.S. railroad system (95%) was converted to diesel engines. Varying degrees of exposure to DP (from 17 $\mu g/m^3$ for clerks to 134 $\mu g/m^3$ for locomotive shop workers) has been reported based upon job groups (Woskie *et al.* 1988a).

Diesel engines have been, and continue to be, commonly used in U.S. mines since their first introduction in the early 1950s. Exposure occurs from activities such as blasting, in which drillers and other heavy machinery using diesel are used. Holland (1978; cited by IARC 1989) conducted an exposure study in 24 U.S. coal mines and showed that, while certain PAH expected from DP were found (anthracene and phenanthrene), other PAH (benz[*a*]anthracene, benz[*a*]pyrene, benz[*e*]pyrene, chrysene, and pyrene) were not found "in measurable quantities. Cornwell (1982; cited by IARC 1989) found other PAH not found in Holland's study in diesel emissions from a molybdenum mine in Colorado. This mine was equipped with drills and various load haul-dumps.

Bus repair facilities were studied to determine diesel exhaust emissions (Apol 1983; cited by IARC 1989). The highest exposure levels were observed when buses were started at peak times of dispatch and return. Pryor (1983; cited by IARC 1989) studied area levels of DP at a bus garage. Elevated levels of diesel exhaust emissions were observed during peak hours of bus activity. Levels rapidly returned to normal 10 to 15 minutes after the passing of peak times.
Using elemental carbon, Zaebst *et al*. (1991) found an effective way of determining truck drivers' exposure to DP. Temperature played an influential role such that higher temperatures are related to higher levels of exposure. This study showed no discernible difference between the exposure levels of truckers (3.8 $\mu g/m^3$) and highway background concentrations (2.5 $\mu g/m^3$). These results would indicate that the truck is not the cause of the truck driver's exposure; rather, it is the highway environment (Zaebst et al. 1991).

Firefighters in three major cities (New York, NY; Boston, MA; and Los Angeles, CA) were studied to determine exposure to DP. To measure total exposure to airborne particles, pumps with filters to trap a methylene chloride soluble fraction were used to evaluate personal exposure. Mostly nonsmokers were used, but the 14% who were smokers averaged higher concentrations of airborne particles (62.6 $\mu g/m^3$ more) than their nonsmoking counterparts. Sampling was performed only when firefighters were in the fire stations. For the three cities, total airborne particulate exposure had a TWA ranging from below 100 $\mu g/m^3$ to 480 $\mu g/m^3$. Froines *et al.* (1987) estimated an average particulate exposure of 300 $\mu g/m^3$ in Boston and New York. With an adjustment for background levels and smoking (75 $\mu g/m^3$), firefighters in these two cities were said to be exposed to a total DP level of 225 $\mu g/m^3$. Los Angeles had the worst conditions of the three cities. Samplings allowed for a "worst-case" scenario in which the mean concentration levels were as high as 748 $\mu g/m^3$. The authors noted that these were busy fire stations located in large metropolitan areas. Other factors such as smoking, building design, age and maintenance of vehicles, activities of the firefighters, and timing of runs also affect results (Froines *et al.* 1987).

Three studies reviewed by International Agency for Research on Cancer (IARC) (1989) found that toll booth workers had elevated levels of exposure to carbon monoxide (CO) (although this was decreased with ventilation systems) and DP. CO exposure was also elevated among border-station and motor vehicle inspectors and parking garage attendants (IARC 1989). In many of these studies, however, it was difficult to differentiate between gasoline exhaust and diesel exhaust. Numerous studies have combined the two exhausts together making exact determinations of DP exposure difficult.

REGULATIONS

There is no published U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for diesel exhaust. OSHA is developing an action plan to reduce worker exposures to this hazard but currently is not initiating rulemaking.

In 1982, the U.S. Environmental Protection Agency (EPA) implemented emission standards for light-duty and heavy-duty diesel vehicles (the emission standards are presented in Tables 1 and 2 (for Light-duty) and Table 3 (for heavy-duty vehicles).

Table 1 and 2. EPA Tier 1 Emission Standards for Passenger Cars and Light-Duty Trucks, FTP 75 (in g/mi)

Category	50,000 miles/5 years					
	HC	MHC	O	NO_x(1) diesel	NO_x gasoline	PM
Passenger cars	0.41	0.25	3.4	1.0	0.4	0.08
LDT, LVW <3,750 lb	-	0.25	3.4	1.0	0.4	0.08
LDT, LVW >3,750 lb	-	0.32	4.4	-	0.7	0.08
HLDT, ALVW <5,750 lb	0.32	-	4.4	-	0.7	-
HLDT, ALVW >5,750 lb	0.39	-	5.0	-	1.1	-

Category	100,000 miles/5 years(2)					
	HC	MHC	O	NO_x(1) diesel	NO_x gasoline	PM
Passenger cars	-	0.31	4.2	1.25	0.6	0.10
LDT, LVW <3,750 lb	0.80	0.31	4.2	1.25	0.6	0.10
LDT, LVW >3,750 lb	0.80	0.40	5.5	0.97	0.97	0.10
HLDT, ALVW <5,750 lb	0.80	0.46	6.4	0.98	0.98	0.10
HLDT, ALVW >5,750 lb	0.80	0.56	7.3	1.53	1.53	0.12

(1) – Nox limits for diesels apply to vehicles through 2003 model year

(2) – Useful life 120,000 miles/11 year for all HLDT standards and for THC standards for LDT.

LVW – loaded vehicle weight (curb weight + 300 lb)

ALVW – adjusted LVW (the numerical average of the curb weight and the GVWR)

LDT – light-duty truck

HLDT – heavy light-duty truck (i.e., any light-duty truck rated greater than 6,000 lb GVWR)

Table 3. EPA Emission Standards for Heavy-Duty Diesel Engines, g/bhp-hr

Year	C	O	O_x	PM
Heavy-Duty Diesel Truck Engines				
1990	1.3	15.5	6.0	0.60
1991	1.3	15.5	5.0	0.25
1994	1.3	15.5	5.0	0.10
1998	1.3	15.5	4.0	0.10
Urban Bus Engines				
1991	1.3	15.5	5.0	0.25
1993	1.3	15.5	5.0	0.10
1994	1.3	15.5	5.0	0.07
1996	1.3	15.5	5.0	0.05[1]
1998	1.3	15.5	4.0	0.05[1]

[1] – in use PM standard 0.07

The American Conference of Governmental Industrial Hygienists (ACGIH) convened a committee to discuss the setting of a Threshold Limit Value (TLV) for diesel exhaust. As a result, diesel exhaust was placed on ACGIH's Notice of Intended Changes for 1995/1996 (0.15 mg/m^3) TWA with a designation as a suspected human carcinogen.

The U.S. Mine Safety and Health Administration (MSHA) is currently in the process of developing a proposed rule for limiting the exposure of mine workers to diesel particulate matter. The National Institute for Occupational Safety and Health (NIOSH) issued a Current Intelligence Bulletin (1989) that recommended that "whole diesel exhaust be regarded as a potential occupational carcinogen." In its Bulletin, NIOSH concluded that "though the excess risk of cancer in diesel exhaust exposed workers has not been quantitatively estimated, it is logical to assume that reductions in exposure to diesel exhaust in the workplace would reduce the excess risk." NIOSH recommended that "all available preventive efforts (including available engineering controls and work practices) be vigorously implemented to minimize exposure of workers to diesel exhaust." Regulations are summarized in Volume II, Table B-45.